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DOI: 10.1002/anie.201205260

C–F Activation

Synthesis of Fluorinated Building Blocks by Transition-Metal-Mediated Hydrodefluorination Reactions

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Keywords:
C–F activation · fluorine chemistry · homogeneous catalysis · hydrodefluorination · transition metals

Angewandte International Edition Chemie

The activation and functionalization of carbon–fluorine bonds can be considered as a major challenge in organometallic chemistry. The growing demand for means to introduce fluorine into new materials or into biologically active molecules has inspired the development of diverse synthetic strategies. Hydrodefluorination is regarded as a promising approach to access partially fluorinated building blocks from readily available perfluorinated bulk chemicals. We provide an overview of transition-metal-based complexes and catalysts that were developed to mediate hydrodefluorination reactions. Special emphasis will be placed on discussing the underlying mechanistic patterns and their impact on scope and selectivity. In addition, future requirements for further developing this field will be highlighted.

From the Contents

1. Introduction

The past three decades have seen an enormous emergence of fluorine chemistry as an integral part of synthetic chemistry. This reflects the steadily increasing importance of fluorine-containing pharmaceuticals, imaging agents, agrochemicals, polymers, optoelectronics, and high-performance materials.[1] Whereas the demand for fluorinated molecules continues to grow tremendously, the development of new means to introduce fluorine into complex organic molecules is hardly keeping pace. The transition-metal-mediated synthesis of fluorinated compounds has recently resulted in a renaissance of organometallic fluorine chemistry.[2]

The interest in fluorinated organic molecules is in part due to the unique properties of carbon–fluorine bonds.[3] Fluorine forms the strongest known σ bond to carbon. Its high electronegativity induces a significant ionic bond character resulting in a high polarity, a short bond, a low polarizability, and a low-lying $\sigma^*_{C\text{-}F}$ antibonding orbital. Fluorine substituents are weak Lewis bases and fluoride is a poor leaving group. These features add up to a high thermodynamic stability and often to a kinetic inertness of carbon–fluorine bonds, rendering fluorination a versatile tool for altering the electron-density distribution in a molecule without a drastic impact on steric parameters. Replacement of C–H or C–OH bonds by C–F bonds is frequently exploited for controlling the acidity, lipophilicity, and metabolic stability of functional organic compounds.[1]

Driven by the striking success of fluorine chemistry, various electrophilic, nucleophilic, and radical fluorination techniques have been developed and continue to be the subject of ongoing research.[1,4] Whereas simple perfluorinated bulk chemicals are easily accessible on an industrial scale, the large-scale synthesis of fine chemicals with a defined partial fluorination pattern often relies on the use of fluorinated building blocks. This strategy avoids the functional-group interference expected from applying fluorinating agents to highly functionalized substrates, but is strongly dependent on the availability of suitable fluorine-containing synthons. A promising synthetic approach to access such building blocks is the derivatization of readily available perfluorinated compounds by selective cleavage of carbon–fluorine bonds.[5]

The simplest transformation in this regard is the conversion of a carbon–fluorine bond into a carbon–hydrogen bond. This reaction, commonly referred to as hydrodefluorination (HDF), has been extensively studied and features a unique mechanistic diversity. It has also paved the way for more complex carbon–fluorine bond functionalizations, such as the highly desirable conversion into carbon–carbon bonds (cross-coupling reactions).[5] Despite this long-standing research interest, there is still much room for substantial improvements in terms of its applicability. At present, HDF is scarcely used for synthetic applications because of the high cost of most reagents and catalysts.

This Review shows the progress in C–F activation reactions by critically analyzing the literature on transition-metal-mediated hydrodefluorination. Examples of heterogeneous,[6] gas-phase,[7] and microbial[8] C–F activation reactions are beyond the scope of this Review. We attempt to derive mechanistic patterns in order to provide a systematic understanding of the metal complexes' structural prerequisites to achieve a good performance and selectivity. Since HDF products are to be used as building blocks for introducing fluorinated functionalities to access compounds of higher value, reactions that lead to complete hydrodefluorination will be excluded. However, selected examples of intramolecular HDF will be presented. A broad overview of C–F

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activation reactions including HDF is given in previous Review articles.[5]

2. Fundamental Aspects

2.1. Thermodynamics

The high carbon–fluorine bond dissociation energy (BDE) of approximately $(500 \pm 50)\ kJ\,mol^{-1}$ requires a thermodynamic compensation for C–F cleavage to occur.[9] Because carbon–hydrogen bond formation is not sufficiently exothermic (BDE approximately $(400 \pm 50)\ kJ\,mol^{-1}$), the necessary compensation is achieved by the formation of a thermodynamically favorable element–fluorine bond; suitable elements include H, Si, B, Sn, and Al as well as the transition metal itself (Figure 1).

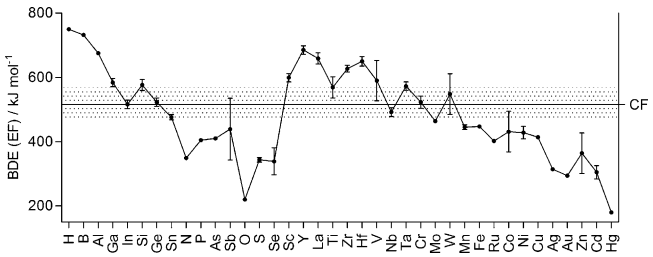

Figure 1. Bond dissociation energies (BDE) of selected diatomic EF molecules taken from Ref. [9].

2.2. The Hydrogen Source

Generating C–H bonds requires a hydrogen source. Frequently, the hydrogen source also provides the fluorine acceptor moiety, as is the case for hydrosilanes R_3SiH. From an atom economical point-of-view, the use of dihydrogen for this purpose is very attractive; in addition, H_2 is inexpensive, readily available, and potentially derived from sustainable sources. However, H_2 is often less reactive than other hydrogen sources; concomitant formation of hydrogen fluoride during HDF can interfere with reactants and reaction vessels. At present, H_2 is scarcely used as hydrogen source.

2.3. Selectivity

The first reported C–F activation reactions required forcing conditions and often led to product mixtures and complete defluorination of the substrate.[5] For practical applications, selectivity is of fundamental importance. Chemoselectivity between fluorine substituents in different environments (e.g. aromatic versus aliphatic HDF) has been frequently observed, arising in part from the differences in C–F bond stability and kinetic inertness; since C–F bond strengths tend to decrease with a lower degree of fluorination, controlling consecutive hydrodefluorination steps can be difficult. Additionally, competition between C–F and C–X bond activation is a common problem (X = H, halogen). Achieving high regioselectivities is more challenging, but has recently received increasing attention. As most biologically relevant molecules bear one or more stereocenters, stereoselective HDF is highly desirable but at present limited to a very few examples.

2.4. Reaction Profiles

For a given transition-metal complex, the relative energies of metal–fluorine, metal–carbon, and metal–hydrogen bonds, as well as the redox properties of the complex, have a decisive impact on the C–F activation reaction's overall feasibility as well as on its primary products and on the mechanistic pathways. Four different reaction profiles for the intermolecular transition-metal-mediated hydrodefluorination were distinguished (Table 1),[51] these are, fluorido complex formation, metal–carbon bond formation, oxidative addition, and reduc-

Table 1: Reaction profiles for intermolecular hydrodefluorination reactions ([M] = transition-metal complex fragment, E = fluorophilic ligand).

Profile	General equation
Fluorido complex formation	$[M]{-}H \xrightarrow{R-F} F{-}[M] + R{-}H$
Metal–carbon bond formation	$[M]{-}E \xrightarrow{R-F} R{-}[M] + E{-}F$
Oxidative addition	$[M] \xrightarrow{R-F} R{-}[M]{-}F$
Reductive hydrodefluorination	$\frac{2}{n}[M]^{N} \xrightarrow{R-F} \frac{2}{n}[M]^{N+n} + R^- + F^-$

Moritz F. Kuehnel studied chemistry at the Freie Universität Berlin. He finished his doctoral studies in 2011 under the supervision of Dieter Lentz in the field of metal hydride-induced hydrodefluorination of alkenes and allenes. After postdoctoral work with Thomas Braun at the Humboldt-Universität zu Berlin, he recently joined the group of Erwin Reisner in Cambridge (UK) as a postdoctoral fellow. For his thesis he received the 2011 Schering Prize. His research is focused on small-molecule activation at transition-metal complexes.

Dieter Lentz studied chemistry at the Ruprecht-Karls-Universität Heidelberg, where he received his Ph.D. in 1979 under the supervision of Konrad Seppelt. After his habilitation at the Freie Universität Berlin in 1986, he was a visiting professor at the Clemson University (USA) in 1991. In 2005 he became an apl. Professor at the Freie Universität Berlin. In 2011, he received the GDCh Fluorine Chemistry division Publication Prize. His main interests are organometallic, fluorine and isocycanide chemistry, homogeneous catalysis, experimental charge density determination and hydrogen storage materials.

tive hydrodefluorination. Conversions were classified according to these profiles, although this classification is not always unambiguous.

3. Fluorido Complex Formation

Hydrogen/fluorine exchange involving hydrido complexes and fluorinated substrates is a feasible route to hydrodefluorination, provided that the concomitant fluorido complex formation is sufficiently exothermic to induce the C–F bond cleavage. The high affinity of early transition metals towards a fluorido ligand is well documented, and consequently this reaction profile is typically observed for Group 4 reagents. Induction of aromatic,[10] vinylic,[11] and aliphatic[10c,g] HDF by zirconium and hafnium hydrido complexes was thoroughly studied by Jones et al. and it was shown that it can involve a plethora of mechanisms.[5n]

3.1. Aromatic Substrates

A number of per- and polyfluoroarenes undergo stoichiometric HDF upon treatment with zirconocene hydrido complexes at elevated temperatures. Mechanistically, these reactions are believed to proceed via a nucleophilic attack of a hydrido ligand at the electrophilic substrate. A concerted σ-bond metathesis mechanism via the four-centered transition state **2** was suggested for the HDF of hexafluorobenzene at $[\{Cp_2Zr(H)_2\}_2]$ (**1**, Scheme 1, $Cp = \eta\text{-}C_5H_5$).[10b] In contrast, the more sterically crowded and less Lewis acidic decamethyl analogue $[Cp^*_2Zr(H)_2]$ (**4**, $Cp^* = \eta\text{-}C_5Me_5$) is assumed to react according to the S_NAr mechanism, in which hydride addition generates a Meisenheimer-type intermediate **5** followed by fluoride transfer to zirconium (Scheme 1).[10c,d] Consequently, the observed selectivities resemble those of classical nucleophilic aromatic displacement reactions, that is, perfluorotoluene and perfluorobiphenyl react at the 4-position, perfluoronaphthalene at the 7-position, and pentafluorobenzene yields a mixture of 1,2,3,4- and 1,2,4,5-$C_6F_4H_2$.

While high metal–fluorine bond strength is a thermodynamic prerequisite for this profile, development of a catalytic process was hampered by the challenging reconversion of

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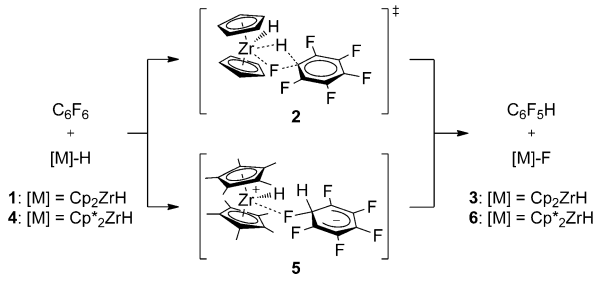
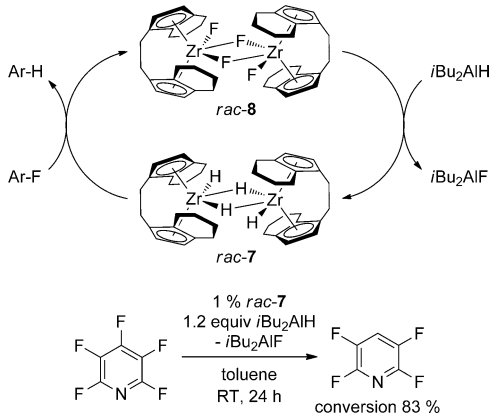


Scheme 1. HDF mechanisms at closely related metal complexes: σ-bond metathesis (top) versus S_NAr (bottom); note that **1** is dimeric in the solid state.

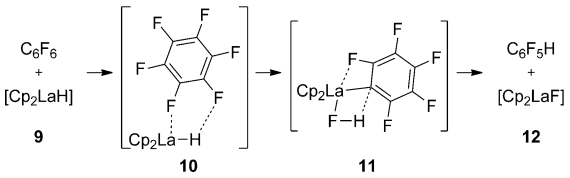
stable fluorido complexes into the corresponding hydrido complexes. Rosenthal et al. showed that aluminum hydrides can serve as regenerating hydride sources for this purpose,[12] thus allowing for catalytic HDF of pentafluoropyridine at room temperature (Scheme 2).[10e] Again, ligand variations



Scheme 2. Catalytic HDF by fluorido complex formation. Top: Schematic representation of the catalytic cycle; bottom: Application to pentafluoropyridine.

have a strong impact on this system: Whereas **1** forms a zirconium pyridyl byproduct, the *ansa*-metallocene **7** efficiently catalyzes the HDF with up to 67 turnovers and a high selectivity for a reaction at the 4-position (Scheme 2).

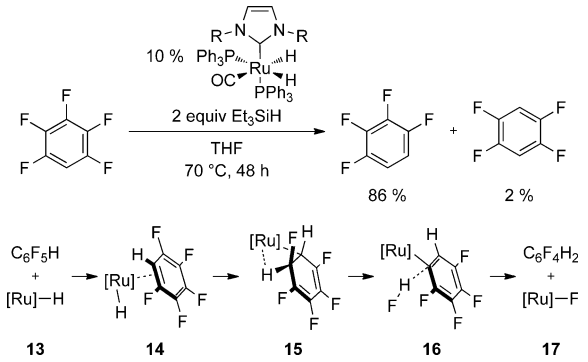
A completely different mechanism was reported for the H/F exchange involving $[(C_5H_2tBu_3)_2CeH]$ and hexa- or pentafluorobenzene.[13] DFT calculations on the related $[Cp_2LaH]$ (**9**) model system indicate that the substrate is "hooked" to the metal center by coordination of a fluorine lone pair (**10**; Scheme 3). The hydrido ligand then interacts



Scheme 3. HDF by the "harpoon" mechanism.

with an *ortho*-fluorine substituent to form hydrogen fluoride and a metal–carbon bond (**11**). Subsequent intramolecular protonolysis of this bond by coordinated HF liberates the HDF product and yields the fluorido complex **12**. The necessary umpolung of the *ipso*-carbon and the hydrido ligand from $C^{\delta+}$ to $C^{\delta-}$ and $H^{\delta-}$ to $H^{\delta+}$, respectively, is believed to account for the high activation barrier to C–F cleavage. Exploiting this harpoon-like mechanism might offer a new approach to *ortho*-selective HDF of functionalized fluoroarenes.

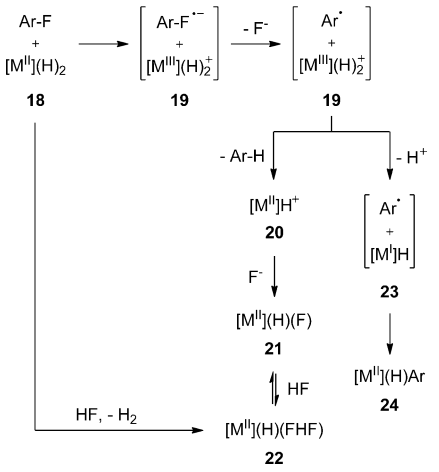
It is consistent with the decreasing metal–fluorine bond energies of more electron-rich metal centers that several Group 6[14] and 8[15] complexes catalyze aromatic C–F bond activation with silanes as hydride sources. Holland et al. employed diketiminato iron fluorido complexes for this purpose, but their efficiency was limited and high catalyst loadings were required (turnover number, TON 4.5).[15a] Mechanistic studies suggest a Meisenheimer-type or σ-bond metathesis mechanism. Whittlesey et al. have demonstrated that carbene ruthenium hydrido complexes allow for more than 200 turnovers and show a unique *ortho*-regioselectivity in the conversion of pentafluorobenzene into 1,2,3,4-tetrafluorobenzene.[15b] Based on DFT calculations and kinetic studies, this selectivity is attributable to a stepwise mechanism via η^2-complex **14** which is formed by phosphine dissociation and coordination of a non-perfluorinated arene double bond (Scheme 4).[15c] This reactivity contrasts with the harpoon



Scheme 4. Catalytic HDF of pentafluorobenzene at ruthenium carbene complexes (R = 2,6-(*i*Pr)$_2$C$_6$H$_3$; [Ru] = [Ru(IMes)(PPh$_3$)(CO)H]; IMes = 1,3-dimesitylimidazol-2-ylidene.

mechanism, in which the d^0 metal center favors formation of a σ-complex (**10**). Subsequent migratory insertion forms an alkyl species **15** which is stabilized by an agostic interaction. α-HF elimination from **15** yields the aryl complex **16**. HF remains loosely attached and induces protonolysis of the ruthenium–carbon bond to afford tetrafluorobenzene and the ruthenium fluorido complex **17**. The calculations suggest a strong influence of the ligand and substrate structure on the activation barrier and selectivity. It is noteworthy that on replacement of the monodentate PPh_3 ligands by a chelating dppp ligand (dppp = $Ph_2P(CH_2)_3PPh_2$)), the reaction outcome is completely changed.[16] In this case, only trace amounts of HDF products could be detected with a ruthenium fluoroaryl complex and hydrogen fluoride being the main reaction products. The bidentate ligand's chelate effect might be responsible for the altered profile, because phosphine dissociation is required for η^2-coordination within the aforementioned mechanism.

The low-lying LUMOs of fluoroaromatics can enable facile electron transfer from electron-rich metal centers (see Section 6). Pioneering work by Clark et al. showed that [*trans*-Pt(H)$_2$(PCy$_3$)$_2$] (**18-Pt**; Cy = cyclohexyl) reacts with a number of fluorinated benzonitriles via radical intermediates (Scheme 5);[17] a very similar mechanism was later

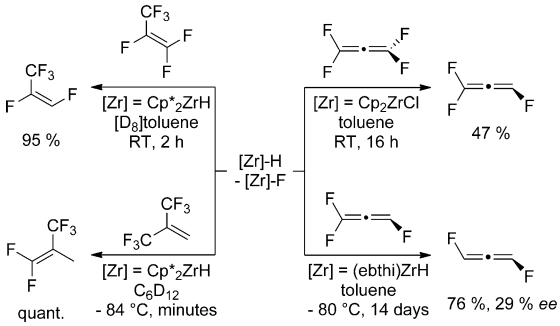


Scheme 5. Fluoroarene HDF by competing radical mechanisms ([M] = Pt(PCy$_3$)$_2$, Ru(dmpe)$_2$; dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$).

proposed by Perutz et al. for the low-temperature fluoroarene activation using [*cis*-Ru(dmpe)$_2$(H)$_2$] (**18-Ru**).[18] Initial single-electron transfer is believed to yield a solvent-caged radical ion pair comprising a cationic dihydrido complex **19** and an aromatic radical anion, which is prone to fluoride loss. In accordance with trapping experiments, an aryl radical is formed and assumed to abstract a hydrogen atom from **19**. The resulting monohydrido cation **20** finally combines with previously expelled fluoride to give the hydrido fluorido complex **21** or a bifluoride complex **22** by reaction with hydrogen fluoride. HF originates from a competing pathway which involves a deprotonation of the cation **19** followed by recombination of the resulting monohydrido species **23** with the aryl radical to give a fluoroaryl complex **24**. It is possible that only the latter pathway is active, because **22** can also be formed by reaction of **18** with HF, as demonstrated in an independent experiment. Another radical mechanism was proposed for the HDF of hexafluorobenzene using [(C$_5$H$_4$Me)$_3$U*t*Bu].[19] In these radical mechanisms, the regioselectivity is determined by the preferred localization of the unpaired electron in the intermediate radical anion, that is, in pentafluorobenzonitrile cleavage of the *para*-C–F bond is observed; this aspect renders attempts to control the selectivity by variation of the metal complex unpromising.

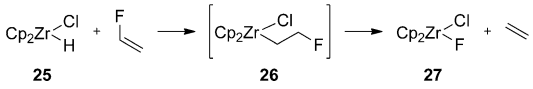
3.2. Olefinic Substrates

The hydrodefluorination of allylic and vinylic fluorides has also been achieved by the formation of fluorido complexes. A broad range of fluoroalkenes were shown to undergo stoichiometric reactions with Group 4 hydrido complexes under very mild conditions (Scheme 6).



Scheme 6. Examples of stoichiometric HDF reactions mediated by zirconium hydrido complexes (ebthi = 1,2-bis(4,5,6,7-tetrahydro-1H-inden-1-yl)ethane-1,2-diyl).

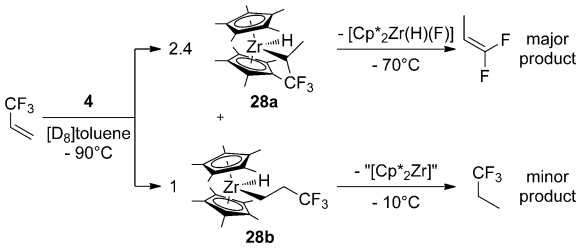
Two competing mechanisms were discussed in the literature. Room-temperature HDF of di- and monofluoroethene using Schwartz' reagent $[Cp_2Zr(H)(Cl)]$ (**25**) was shown by Caulton et al. to proceed by a two-step insertion–elimination mechanism.[20] Without prior metal coordination, fluoroethene inserts into the zirconium–hydrogen bond to give a fluoroethyl intermediate **26** (Scheme 7); subsequent β-



Scheme 7. The insertion–elimination mechanism for the HDF of fluoroalkenes.

fluoride *syn* elimination affords ethene and the zirconium fluorido complex **27**. The conceivable stabilizing effect of β-agostic Zr–F interactions was calculated to be negligible. Joint mechanistic studies by the research groups of Jones and Eisenstein suggest a very similar reaction coordinate for the HDF of perfluoropropene by $[Cp^*_2Zr(H)_2]$ (**4**), however, involving η^2-coordination prior to insertion.[11a]

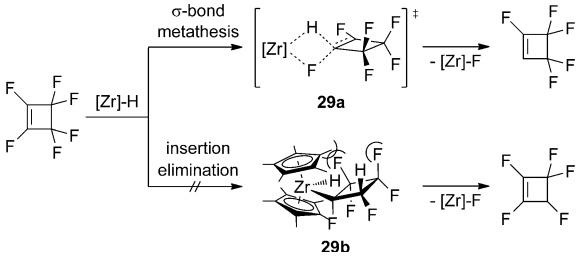
The hydrido ligand's nucleophilic character determines the HDF regioselectivity by preferential attack at the most electrophilic site in the molecule, resembling typical nucleophilic displacement reactions. This is reflected in the substrate's overall reactivity, which correlates with its electrophilicity. Since the electrophilicity depends strongly on the degree of fluorination, remarkable selectivities were achieved in stoichiometric reactions. Thus, a selective conversion of hexafluoropropene into *E*-1,2,3,3,3-pentafluoropropene was observed with one equivalent of $[Cp^*_2Zr(H)_2]$ (**4**), whereas an excess of the hydrido complex leads to undesired complete hydrodefluorinations or complex product mixtures. HDF of the less-electrophilic 3,3,3-trifluoropropene at low temper-



Scheme 8. The formation of different intermediates determines the product distribution in the HDF of trifluoropropene.

atures allowed the detection of intermediates that account for the lower selectivity frequently observed for allylic substrates (Scheme 8):[11c] Markovnikov addition of **4** to the double bond generates the intermediate **28a** which is capable of β-fluoride elimination from the CF_3 group to furnish 1,1-difluoropropene upon warming. In contrast, **28b** which is formed by anti-Markovnikov addition, has no fluorine in β-position to the metal and cannot form a fluorido complex; instead, decomposition at higher temperature yields the hydrogenation product 1,1,1-trifluoropropane. The observed ratio of intermediates **28a**/**28b** is in accordance with the final product distribution.

Cyclic substrates were shown to react by a concerted σ-bond metathesis mechanism via four-centered transition state **29a** (Scheme 9). Quantum mechanical calculations revealed

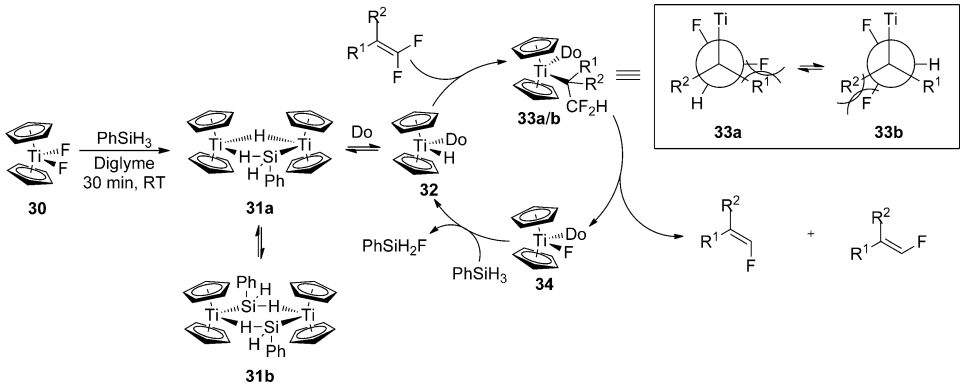


Scheme 9. The σ-bond metathesis mechanism is favored over an insertion elimination mechanism for the HDF of cyclic alkenes at zirconium hydrido complexes ([Zr] = Cp^*_2ZrH).

only a relatively small energetic difference between the insertion–elimination and σ-bond metathesis pathways; again, it is not surprising that minor alterations in the reagent structure and the substrate have a strong impact on the favored mechanism. The carbocyclic moiety's high steric demand in the insertion product **29b** makes the insertion–elimination mechanism unfavorable, this effect is particularly pronounced for $[Cp^*_2Zr(H)_2]$.[11b] $[Cp^*_2Zr(H)(F)]$ (**6**) was found to be incapable of olefin insertion, making σ-bond metathesis the only feasible path.[11b,c]

In addition, zirconium hydrido complexes are also suitable for the HDF of fluoroallenes and offer a new synthetic route to the otherwise hardly accessible trifluoroallene and 1,3-difluoroallene.[21] A chiral zirconium hydrido complex was shown to yield optically active 1,3-difluoroallene from trifluoroallene, thus demonstrating the first example of an asymmetric C–F activation (Scheme 6).

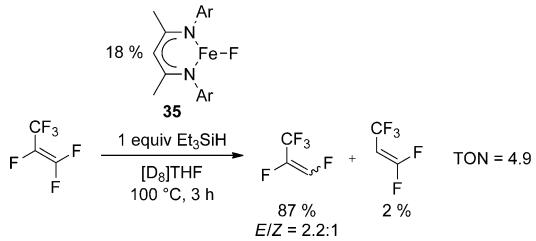
Replacing zirconium by hafnium has no significant effect apart from reducing the reactivity,[10f] whereas moving to related titanium complexes weakens the metal–fluorine bond so that catalytic HDF becomes possible. Lentz et al. showed that a broad range of fluoroalkenes undergo H/F exchange with various silanes in the presence of catalytic amounts of $[Cp_2TiF_2]$ (**30**), achieving a maximum TON of 125 and a benchmark turnover frequency (TOF) of 1500 h^{-1}.[22] Despite having a strong resemblance to the zirconium complexes, the titanium complexes are less reactive and less selective. Whereas fluoropropenes react at ambient temperature, fluorinated styrenes require more forcing conditions; fluoroethenes are hardly reactive. As seen with zirconium complexes, allylic HDF competes with undesirable hydrogenation and is generally much slower than vinylic HDF. Mechanistic studies indicate a Ti^{III} hydrido complex **32** as the active species which is formed in situ from the Ti^{IV} fluorido precatalyst and the silane (Scheme 10).[22b,c] In contrast to the



Scheme 10. Catalytic cycle for the titanium-catalyzed HDF of fluoroalkenes (Do = donor solvent; R^1, R^2 = aryl, alkyl, H, F).

Zr analogue, varying *E*/*Z*-selectivities were observed and rationalized on the basis of conformational effects in the putative intermediates **33a/b** within the assumed insertion elimination mechanism:[22c] β-Fluoride elimination proceeds through a *syn* geometry forcing one of the substituents R^1 (**33a**) or R^2 (**33b**) into an eclipsed conformation with a vicinal fluorine substituent; the relative sizes of R^1 and R^2 determine the preferred rotational isomer and thus the product configuration, for example, *E*:*Z* = 94:6 for R^1 = H, R^2 = CF_3; *E*:*Z* = 40:60 for R^1 = H, R^2 = CH_3. For perfluorocyclobutene, both the σ-bond metathesis and insertion–elimination mechanisms were found to be operative.

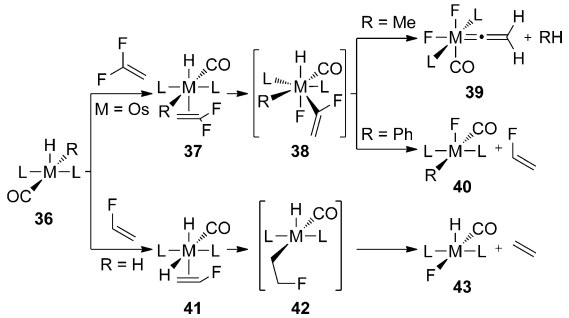
Despite the lower metal–fluorine bond energies of electron-rich transition metals, a number of Group 8 metal hydrido complexes induce vinylic HDF with concomitant formation of fluorido complexes. Holland's low-coordinate iron fluorido complex **35** catalyzes the HDF of hexa- and trifluoropropene employing triethylsilane as the hydride source. Up to five turnovers were observed (Scheme 11).[15a] Spectroscopic data suggest an Fe^{II} hydrido complex as the active species which reacts by the insertion–elimination mechanism. The observed formation of 1,1,3,3,3-pentafluoropropene is noteworthy in that it contrasts with all the



Scheme 11. Iron-catalyzed HDF of hexafluoropropene (Ar = 2,6-($iPr_2C_6H_3$).

aforementioned reagents, which show an exclusive reactivity towards the terminal carbon atom. This lowered selectivity might be attributable to the confined space between the ligand's bulky aryl groups, making the electronically disfavored yet sterically more accessible addition of the metal to the terminal carbon atom feasible. Since steric congestion in this system is documented by the inactivity of a bulkier *tert*-butyl analogue, it seems likely that systematic variations on the steric demand of the ligand can be exploited to influence the selectivity.

Caulton et al. studied ruthenium and osmium hydrido complexes that undergo H/F exchange with mono- and difluoroethene in stoichiometric reactions.[23] The chosen metal center as well as the ligand system has a strong influence on the mechanistic outcome (Scheme 12): Carbon–fluorine bond oxidative addition to complexes **36** is believed to yield the Os^{IV} intermediate **38** that exhibits two options for further reactions. For R = methyl, reductive elimination of methane followed by a second C–F oxidative addition is observed to yield the vinylidene species **39**. For R = phenyl, reductive elimination of fluoroethene is favored affording the Os^{II} fluorido complex **40**. Ruthenium analogues (R = Ph, Me) always follow the reductive elimination/oxidative addition



Scheme 12. Competing mechanisms observed at osmium and ruthenium hydrido complexes (L = $PtBu_2Me$; M = Ru, Os; R = H, Me, Ph).

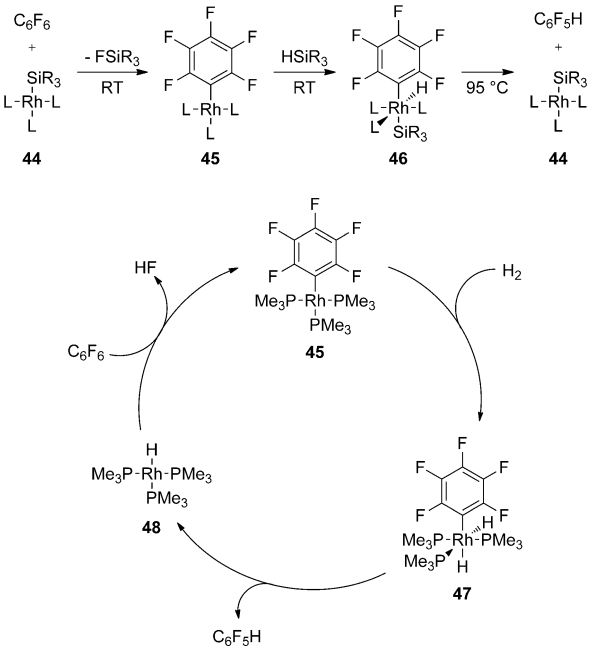
path to give vinylidene species. These differences were attributed to the ease of CH_4 formation in contrast to C_6H_6 formation and the higher stability of high oxidation states of osmium than of ruthenium. In contrast, the dihydrido complexes (R = H, M = Ru, Os) react with fluoroethene by the insertion elimination mechanism. A related octahedral dihydrido complex [*cis*-Ru(dmpe)$_2$(H)$_2$] (**18b**) was shown to mediate regioselective HDF of hexafluoropropene to give pentafluoropropene (E/Z = 1:4) and tetrafluoropropene as well as a ruthenium bifluoride complex [*cis*-Ru(dmpe)$_2$F-(F···HF)].[24] No mechanistic details were reported.

4. Metal–Carbon Bond Formation

Lowering the metal center's fluorine affinity beyond a certain degree can render the formation of a metal–fluorine bond energetically disfavored over formation of a metal–carbon bond, especially because σ bonds to fluorinated carbon atoms are often more stable than σ bonds to analogous hydrocarbon moieties.[25] To form a metal–carbon bond by C–F bond cleavage, concomitant formation of a strong element–fluorine bond has to provide the thermodynamic driving force. Typical elements with a high affinity towards fluorine are hydrogen, silicon, and boron. In a subsequent step, hydrogen transfer from an external hydrogen source to the carbon atom cleaves the metal–carbon bond and liberates the HDF product. This two-step mechanism via sometimes isolable organometallic intermediates offers a number of strategies for further functionalizing the metal-bound fluorocarbon moiety beyond hydrodefluorination.

4.1. Aromatic Substrates

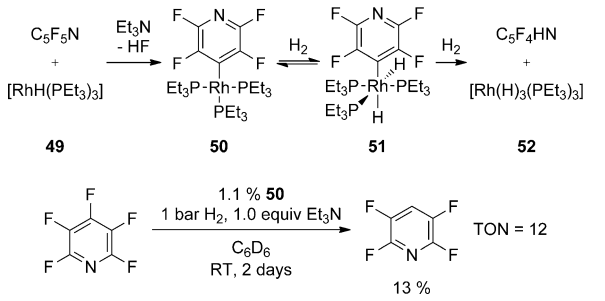
A hydrodefluorination of fluoroarenes using rhodium complexes was introduced by the Milstein group.[26] Formation of a stable silicon–fluorine bond promotes the reaction of the rhodium(I) silyl complex **44** with hexafluorobenzene to afford the fluoroaryl complex **45** and the corresponding fluorosilane. The rhodium–carbon bond in **45** is subsequently cleaved by reaction with a hydrosilane to yield pentafluorobenzene and to regenerate the silyl complex **44** by Si–H oxidative addition and C–H reductive elimination (Scheme 13). This reactivity was further exploited and led to the development of the first catalytic cycle for the HDF of C_6F_6 and C_6F_5H to give C_6F_5H and 1,2,4,5-$C_6F_4H_2$, respectively, with up to 38 turnovers.[26a] When concomitantly formed hydrogen fluoride is trapped by addition of a base, less costly dihydrogen can replace the hydrosilanes (Scheme 13), and this catalytic system is also more efficient (TON up to 114).[26b] A rhodium(I) hydrido complex **48** was identified as the active species in this process. Based on the observed preference for C–F activation over C–H activation, the correlation between substrate electron affinity and reactivity, and the significantly lower catalytic activity of a less electron-rich precatalyst, it was suggested that the C–F activation step proceeds by an electron-transfer mechanism. An alternative mechanism involving deprotonation and



Scheme 13. Stoichiometric and catalytic HDF of hexafluorobenzene by rhodium phosphine complexes (L = PMe_3; SiR_3 = $SiMe_2Ph$, $SiPh_3$, $Si(OEt)_3$).

subsequent nucleophilic substitution of an aromatic compound by the resulting anionic metal center was also discussed.[27]

The use of Rh^I hydrido complexes for C–F activation by liberation of hydrogen fluoride was further studied by Braun et al.[28] [$RhH(PEt_3)_3$] (**49**) was treated with pentafluoropyridine to yield selectively the 4-tetrafluoropyridyl complex [$Rh(C_5F_4N)(PEt_3)_3$] (**50**, Scheme 14).[28a] Exposing **50** to

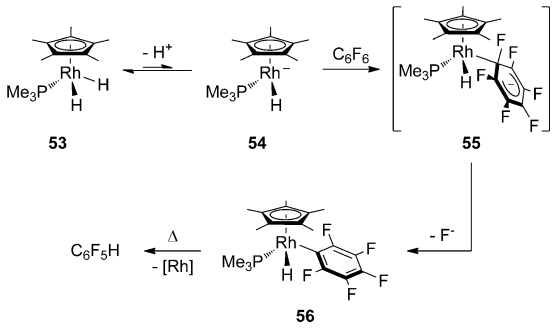


Scheme 14. Hydrodefluorination of pentafluoropyridine using rhodium hydrido complexes.

dihydrogen furnishes initially the dihydrido compound **51** and then 2,3,5,6-tetrafluoropyridine and the Rh^{III} trihydrido complexes **52** (a mixture of the *mer*- and *fac*-isomers), which were formed from **49** by oxidative addition of dihydrogen. Thus **50** can serve as a catalyst for the HDF of pentafluoropyridine with H_2 as the hydrogen source. Up to 12 turnovers were achieved at room temperature (Scheme 14).[28b]

A very different mechanism was observed by Jones et al. for reactions of the half-sandwich Rh^{III} dihydrido complex

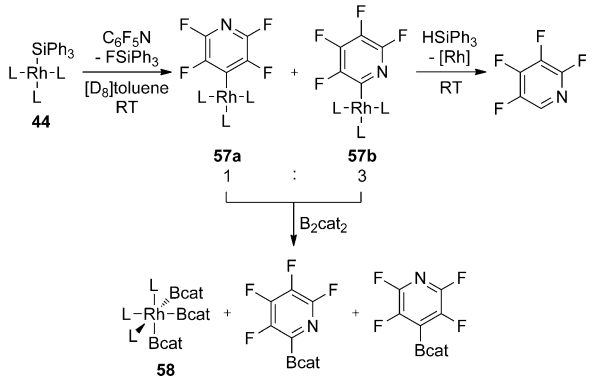
[Cp*Rh(PMe$_3$)(H)$_2$] (**53**) towards perfluoroarenes, such as hexafluorobenzene, pentafluorobenzene, and perfluoronaphthalene.[27] Deprotonation of **53** by an external base generates a Rh^I anion **54** which is capable of a nucleophilic fluoride displacement from the substrate, presumably via a Meisenheimer-type intermediate **55** (Scheme 15). Subsequent ther-



Scheme 15. Hydrodefluorination of hexafluorobenzene by nucleophilic aromatic substitution.

molysis of the resulting aryl complex **56** liberates the HDF product. However, attempts to make this reaction catalytic on using a H_2 atmosphere were barely successful (TON = 1.4).

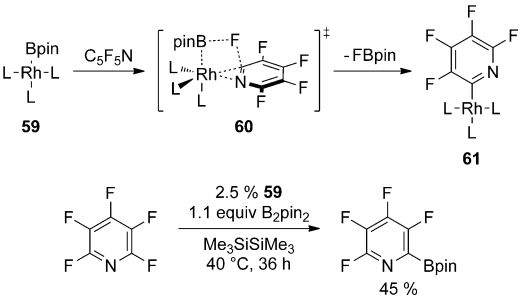
Marder, Perutz et al. demonstrated that the silyl complex **44** also reacts with pentafluoropyridine to afford the isomeric tetrafluoropyridyl complexes **57a** and **57b** in a 1:3 ratio and the corresponding fluorosilane. Notably, an unusual C–F activation at the 2-position is preferred (Scheme 16).[29] Upon



Scheme 16. C–F activation of pentafluoropyridine at a Rh^I silyl complex (L = PMe$_3$; B_2cat_2 = 2,2′-bibenzo[d][1,3,2]dioxaborole).

treatment with triphenylsilane, **57b** liberates the corresponding 2,3,4,5-tetrafluoropyridine, whereas **57a** does not react; the inorganic products of this reaction could not be identified, thus preventing a catalytic process. When the diborane B_2cat_2 (B_2cat_2 = 2,2′-bibenzo[d][1,3,2]dioxaborole) was treated with **57a/b**, a mixture of unprecedented C–F borylation products and the rhodium(III) boryl complex **58** were formed, the rhodium(III) complex presumably via an intermediate Rh^I boryl complex. Although the boron–fluorine bond is even stronger than a silicon–fluorine bond, **58** could not be used as a catalyst for this reaction.

In contrast, Braun et al. succeeded in synthesizing a related Rh^I boryl complex **59**.[30] Upon treatment of **59** with pentafluoropyridine, exclusive C–F activation at the 2-position is observed to afford the 2-tetrafluoropyridyl complex **61** and the corresponding fluoroborane (Scheme 17).

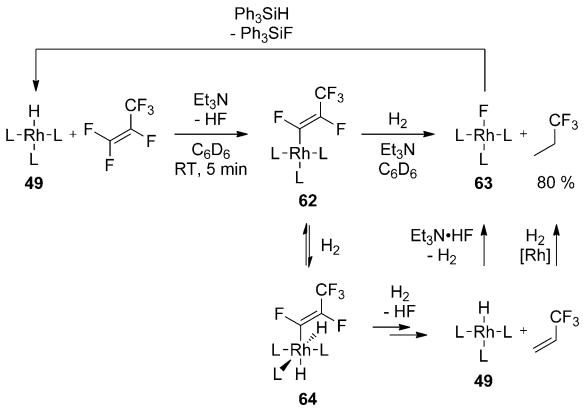


Scheme 17. *ortho*-Selective C–F activation and catalytic borylation of pentafluoropyridine employing a Rh^I boryl complex (L = PEt$_3$; B_2pin_2 = 4,4,4′,4′,5,5,5′,5′-octamethyl-2,2′-bi(1,3,2-dioxaborolane)).

Complex **59** can thus serve as a catalyst for the borylation of pentafluoropyridine at the 2-position to furnish a promising building block for otherwise inaccessible 2-substituted tetrafluoropyridines. DFT calculations by Macgregor et al. on this remarkable selectivity revealed a novel boryl-assisted C–F bond activation mechanism which has some resemblance to previously reported phosphine-assisted mechanisms.[5k,31] A four-membered transition state **60** is formed by attack of the electron-rich rhodium center at the *ipso*-carbon and the interaction of a fluorine lone pair with the boryl ligand. Consistent with the high Lewis acidity of this ligand, **60** could be regarded as a counterpart of transition state **2** (see Section 3.1), in which the Lewis acidic metal coordinates to fluorine while the *ipso*-carbon is attacked by the nucleophilic ligand. An additional stabilizing interaction between the pyridine nitrogen atom and the rhodium center was found to account for the *ortho*-selectivity.

4.2. Olefinic Substrates

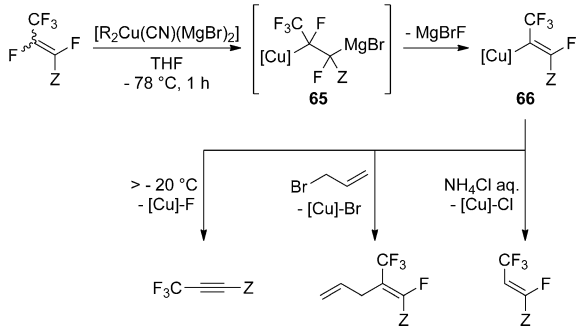
Most transition-metal complexes capable of undergoing C–F bond metalation with fluoroarenes show a comparable behavior with fluoroalkenes. The Rh^I hydrido complex **49** reacts with hexafluoropropene to give selectively the *Z*-pentafluoropropenyl complex **62** and HF, which has to be trapped by triethylamine (Scheme 18).[32] Upon exposure to dihydrogen, **62** undergoes a tandem hydrodefluorination/hydrogenation affording 1,1,1-trifluoropropane as well as the rhodium fluorido complex **63**. Reversible oxidative addition of H_2 to **62** was demonstrated to generate a Rh^{III} dihydrido species **64**, which is presumably an intermediate in the formation of trifluoropropane. Reductive elimination of pentafluoropropene subsequently regenerates **49**. Repeated HDF steps eventually afford 3,3,3-trifluoropropene; hydrogenation of the 3,3,3-trifluoropropene to trifluoropropane is



Scheme 18. Proposed reaction mechanism for the rhodium-mediated hydrodefluorination of hexafluoropropene (L = PEt_3).

catalyzed by **49**. The fluorido complex **63** may for example originate from protonolysis of **49**, **62**, or another intermediate Rh vinyl species by triethylamine·HF[33] and can be reconverted into **49** by treatment with triphenylsilane, thus completing a cyclic process. Replacing dihydrogen by other hydrogen–element reagents allows for C–F bond functionalization beyond hydrodefluorination. In the presence of hydrosilanes, **62** catalyzes the selective formation of 3,3,3-trifluoropropylsilanes (TON up to 90), possibly via intermediate Rh^I silyl species.[34] Using the borane HBpin (HBpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolane), hexafluoropropene is catalytically converted into a mixture of fluoroalkyl dioxaborolanes (TON up to 250, TOF 12.5 h^{-1}).[35] The intermediacy of a Rh^I boryl species was supported by the independent preparation of **59** which is capable of activating hexafluoropropene both at the 2- and 3-position.[30]

A completely different strategy for olefin hydrodefluorination was pursued by the Ishihara group.[36] A low-temperature reaction of organocuprates with functionalized pentafluoropropene derivatives selectively generates the vinyl copper species **66**. The proposed insertion–elimination-like reaction mechanism consists of a copper–magnesium addition to the alkene double bond and subsequent elimination of magnesium bromo fluoride (Scheme 19). Hydrolysis of **66** affords HDF products in high yields. Alternatively, other



Scheme 19. Hydrodefluorination of fluoroalkenes by organocuprate insertion (R = Ph; Z = CO_2Bn, SO_2Tol, S(O)Tol; Bn = benzyl, Tol = tolyl).

electrophiles can be used to functionalize the vinyl moiety. In the absence of a suitable electrophile, **66** decomposes to a trifluoropropyne derivative by β-fluoride elimination. The use of relatively mild cuprate reagents makes this HDF reaction tolerant towards ester and sulfinyl functions.

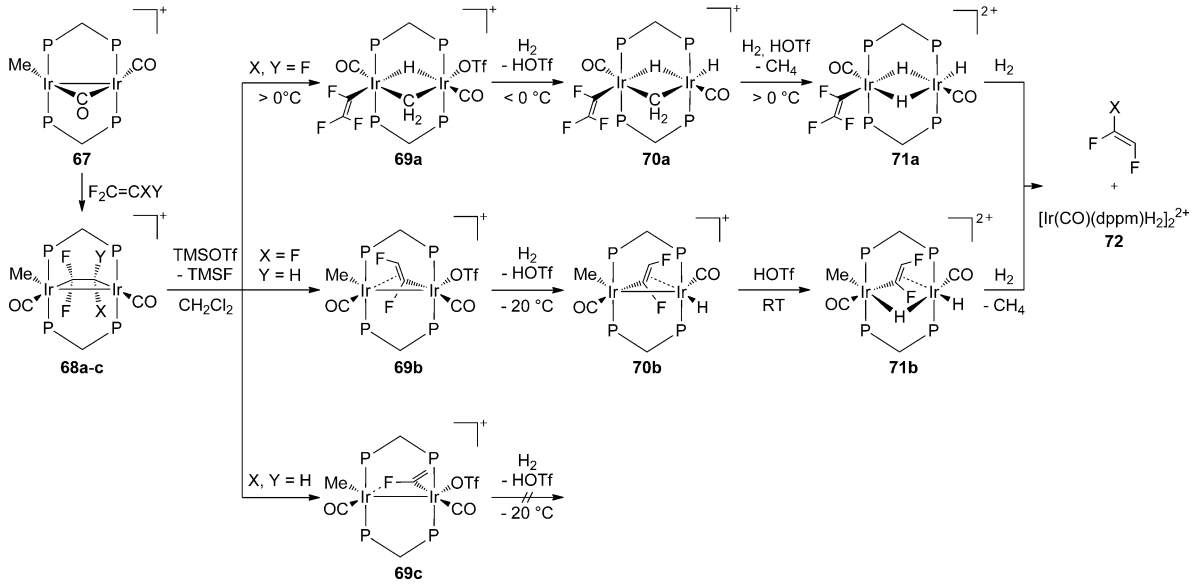
The 1,2-dimetallated alkane **65** resembles an olefin in a bridging coordination site between a pair of metal centers.[37] Cooperative carbon–fluorine bond activation by two adjacent metal centers was also investigated by Cowie et al.[37] The cationic dinuclear iridium complex $[Ir_2(Me)(CO)_2dppm_2][OTf]$ (**67**, dppm = $(Ph_2P)_2CH_2$) forms μ_2-η^1:η^1 complexes **68a–c** with tetra-, tri-, and difluoroethene, which are susceptible to fluoride abstraction with Lewis acids at low temperatures (Scheme 20). The resulting tri-, di-, and monofluorovinyl complexes **69a–c** differ in their vinyl moieties adopting either a terminal η^1 (**69a**), a bridging μ_2-η^1:η^2 (**69b**), or a bridging μ_2-η^1:η^1 (**69c**) coordination mode. At low temperatures, **69a** and **69b** react with dihydrogen to afford hydrido complexes **70a**,**b**, whereas **69c** shows no comparable reactivity. Upon warming, successive hydrogenolysis eventually furnishes the hydrodefluorination products and a dimeric Ir^{III} hydrido complex **72** by oxidative addition of dihydrogen and reductive elimination of methane (Scheme 20).

4.3. Benzylic Fluorides

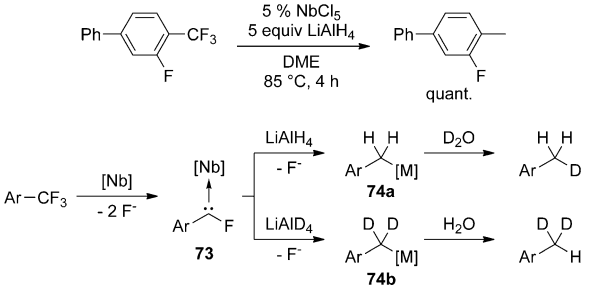
Niobium species were shown by Akiyama et al. to catalyze the H/F exchange at aromatic or benzylic fluorides with lithium aluminum hydride (Scheme 21). Up to 94 turnovers were achieved (TOF = 23.3 h^{-1}).[38] In substrates bearing both aromatic and benzylic fluorine substituents, this catalytic system shows an unusual preference for aliphatic HDF which is reminiscent of HDF at Lewis acidic main-group compounds.[39] Isotopic labeling studies suggest the intermediate formation of a niobium carbene complex **73**. Reaction with $LiAlH_4$ forms a lithium or aluminum benzyl species **74a/b**, which upon hydrolysis affords the HDF product.

5. Oxidative Addition

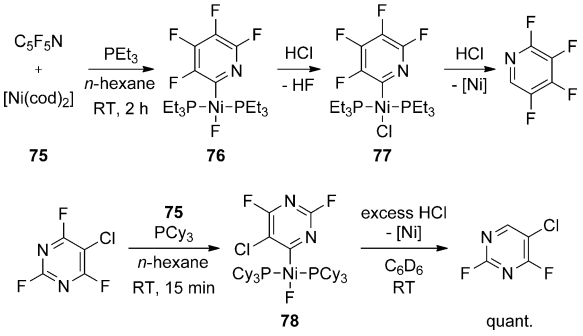
Oxidative addition of carbon–fluorine bonds is among the most studied pathways in transition-metal-mediated C–F bond activation. In a way it relates to both of the previous two reaction profiles in that it involves the simultaneous formation of both a metal–carbon and a metal–fluorine bond. Subsequent replacement of the fluorido ligand by an exogenous hydride source allows for reductive elimination of the hydrodefluorination product. C–F bond functionalization beyond HDF is possible when the fluorido ligand is substituted by other nucleophiles.[5,40] Since this final reductive elimination step regenerates a low-valent metal complex, many reactions via this route require only catalytic amounts of the metal reagent. As a drawback, however, competing activation of C–H bonds is frequently observed.[5e,41] Typically, HDF via oxidative addition is observed at coordina-



Scheme 20. Cooperative hydrodefluorination of fluoroethenes at a cationic dinuclear iridium complex (OTf^- counterions omitted for clarity; P = PPh_2; dppm = $(Ph_2P)_2CH_2$; TMS = $SiMe_3$; OTf = CF_3SO_3).



Scheme 21. Niobium-catalyzed benzylic HDF (M = Li, AlX_2; DME = 1,2-dimethoxyethane).



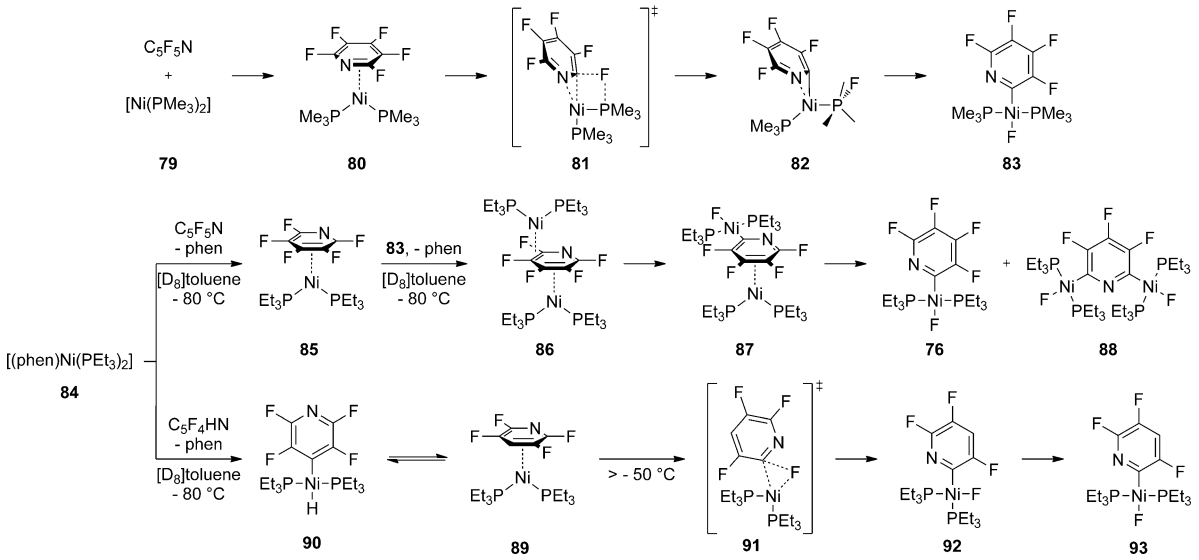
Scheme 22. Selective hydrodefluorination at the *ortho* position of fluorinated heterocycles by C–F bond oxidative addition at nickel complexes (cod = 1,5-cyclooctadiene).

tively unsaturated low-valent late-transition-metal complexes.

5.1. Aromatic Substrates

Although the first report on oxidative addition of fluoroarenes to a nickel(0) complex dates back to the late 1970s,[42] it had not been exploited for HDF until Perutz et al. studied this chemistry in more detail about 20 years later.[43] In the presence of PEt_3, $[Ni(cod)_2]$ (**75**; cod = cyclooctadiene) was found to react with various fluorinated arenes and heteroarenes to afford (aryl)(fluorido)nickel(II) complexes even in the presence of weaker C–H bonds (Scheme 22).[44] The activation of fluoropyridines and fluoropyrimidines proceeds much more rapidly than that of fluorobenzenes with a selectivity for the position *ortho* to nitrogen. Variations on the phosphine employed allow for selective C–F bond activation of 5-chloro-2,4,6-trifluoropyrimidine without affecting the more reactive C–Cl bond. However, this selectivity is not observed for related chlorofluoropyridines.[45] Subsequent protonolysis of the aryl complexes **76** and **78** with excess hydrogen chloride liberates HF and the *ortho*-hydrodefluorinated heterocycles; the chlorido complex **77** was identified as an intermediate in these reactions. A few related examples of HDF at nickel and iridium were reported.[46]

From a mechanistic point of view, these reactions are still under considerable debate. DFT calculations on the oxidative addition of pentafluoropyridine at the model complex $[Ni(PMe_3)_2]$ (**79**) attribute the observed *ortho*-selectivity to a phosphine-assisted reaction mechanism (Scheme 23, top).[31i] The initially formed η^2-arene complex **80** is believed to undergo C–F addition across the nickel–phosphorus bond via a four-membered transition state **81**. Cleavage of the *ortho*-C–F bond is favored because coordination of the pyridine nitrogen atom to the nickel center additionally stabilizes the transition state. The resulting metallaphosphorane **82** is a shallow intermediate and subsequently rearranges to yield the *trans*-pyridyl fluorido complex **83** directly, bypassing a *cis* isomer. Note that phosphine-assisted C–F

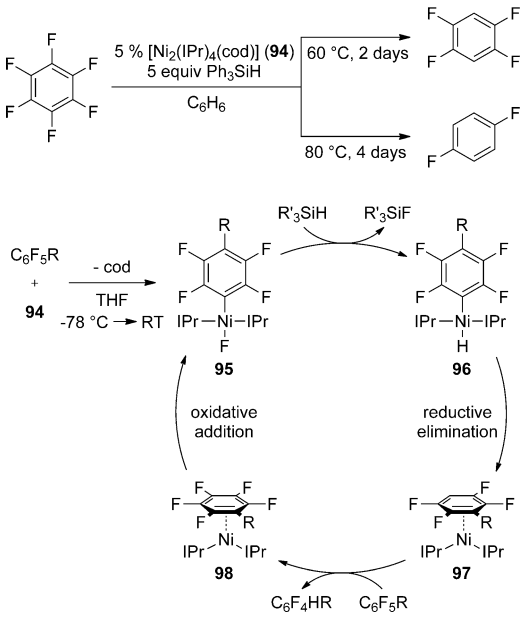


Scheme 23. Top: *ortho*-selectivity in the oxidative addition of pentafluoropyridine by a phosphine-assisted reaction mechanism based on DFT calculations. Bottom: alternative reaction pathways for the activation of penta- and tetrafluoropyridine based on experimental data (phen = phenanthrene).

activation was described before.[5k,31] The energetic difference between this pathway and a concerted oxidative addition was shown to be relatively small and substrate dependent.

Recent experimental studies by Johnson's group on the reaction of a $[Ni(PEt_3)_2]$ synthon **84** with pentafluoropyridine confirmed the formation of a fluxional η^2-arene complex **85**, but also demonstrated the participation of dinuclear complexes **86** and **87** (Scheme 23, bottom).[47] At present, the role of these dinuclear species is not clear, but they are very likely to influence the regioselectivity. Similar studies employing tetrafluoropyridine as the substrate revealed a fast equilibrium between the η^2-arene complex **89** and the C–H oxidative addition product **90** at low temperatures. Upon temperature elevation, *ortho*-C–F oxidative addition was found to yield an unexpected *cis*-pyridyl fluorido complex **92** which slowly isomerizes to the *trans* analogue **93**. Neither the intermediacy of *cis*-**92** nor the low activation barrier derived from kinetic measurements is consistent with a phosphine-assisted mechanism. Instead, a concerted oxidative addition mechanism via the three-centered transition state **91** was proposed. Related mechanistic investigations on hexa-,[48] penta-,[48] and tetrafluorobenzenes[49] similarly demonstrated the involvement of mono- and dinuclear η^2-arene complexes as well as the occurrence of a reversible C–H oxidative addition. In contrast, the use of $[Ni(PEt_3)_4]$ as the Ni^0 source resulted in a much lower selectivity and gave rise to EPR signals indicative of a Ni^I species formed by a single-electron-transfer mechanism.

Based on the application of carbene ligands instead of phosphines, Radius et al. developed a nickel-catalyzed process for the hydrodefluorination of hexafluorobenzene to give selectively 1,2,4,5-tetra- and 1,4-difluorobenzene using silanes as the hydride source (Scheme 24).[50] Mechanistic studies are consistent with an in situ generation of a bis(carbene)nickel(0) complex fragment **94** and subsequent oxidative addition of the substrate to give the *trans*-nickel(II) aryl fluorido complex



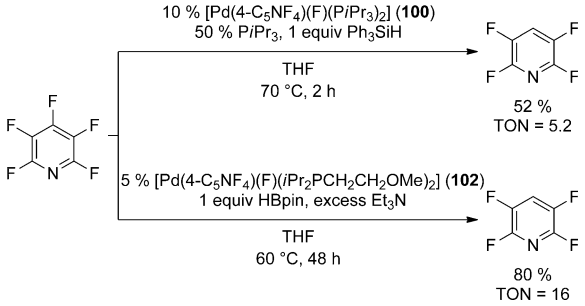
Scheme 24. Catalytic cycle for the nickel-catalyzed HDF of fluorarenes (IPr = 1,3-diisopropylimidazol-2-ylidene; R = F, CF_3; R′ = Et, Ph).

95.[51] Ligand exchange by treatment with triethylsilane yields the corresponding hydrido complex **96**, which is capable of reductive elimination to afford an η^2-complex **97** of the hydrodefluorinated arene. Exchange with another substrate molecule and subsequent oxidative addition regenerate the aryl fluorido complex **95**, thus closing the catalytic cycle. As with the nickel phosphine systems, detailed studies on the C–F activation mechanism revealed some ambiguities: Whereas kinetic data and DFT calculations are consistent with a concerted direct oxidative addition mechanism for the activation of perfluoroarenes,[51b] the observed regioselectivity in the

activation of heptafluorotoluene disagrees with that predicted by DFT calculations.[50]

Further work on both the N-heterocyclic carbene (NHC)[51b,52] and the phosphine[44b,53] systems demonstrated that displacing the fluorido ligand by carbon nucleophiles leads to reductive elimination of a carbon–carbon bond. This reactivity was exploited for nickel-catalyzed cross-coupling of fluoroarenes with stannanes and boronic acids. When stronger hydride reagents, such as borohydrides, are used instead of silanes, the catalyst's activity increases to such an extent, that multiple hydrodefluorination steps are possible.[54] These reactions, however, show little selectivity and often result in a complete hydrodefluorination of the substrate.

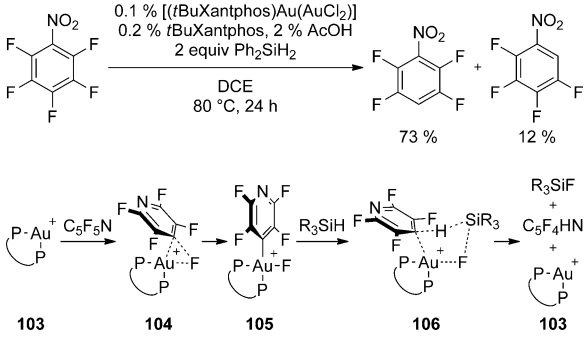
Hydrodefluorination of fluoroarenes by oxidative addition is not limited to nickel and has also been observed at low-valent palladium complexes.[31c] Pentafluoropyridine reacts with $[Pd(P\mathit{i}Pr_3)_2]$ (**99**) to afford *trans*-$[Pd(4\text{-}C_5F_4N)(F)(P\mathit{i}Pr_3)_2]$ (**100**) by cleavage of the C–F bond in the 4-position. In contrast to the analogous nickel complexes, formation of the thermodynamically preferred (4-pyridyl) complex **100** requires elevated temperatures and longer reaction times. Similar to the nickel analogues, the corresponding hydrido complex *trans*-$[Pd(4\text{-}C_5F_4N)(H)(P\mathit{i}Pr_3)_2]$ (**101**) is obtained by treatment of **100** with silanes or boranes and it undergoes reductive elimination of 2,3,5,6-tetrafluoropyridine;[55] a catalytic process derived from this reactivity, however, was found to be rather inefficient (TON = 5.2, Scheme 25). The



Scheme 25. Palladium-catalyzed hydrodefluorination of pentafluoropyridine (HBpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolane).

methoxy-substituted derivative **102** shows an increased activity, so that catalytic HDF proceeds at a lower temperature and with a higher efficiency (TON = 16).[56] Other catalytic functionalizations of pentafluoropyridine were also achieved. At present, there is little mechanistic knowledge,[57] especially the role of the methoxy-function remains unclear.

Recently, Zhang and co-workers reported the catalytic HDF of electron-deficient perfluoroarenes in the presence of a gold(I) catalyst.[58] This catalytic system uses silanes as the hydrogen source and is exceptionally tolerant towards functional groups such as keto, carboxylate, nitrile, alkynyl, alkenyl, nitro, and amide groups. Based on a systematic optimization, a benchmark TON of 1000 was achieved, when additional Xantphos (Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene) and a proton source were

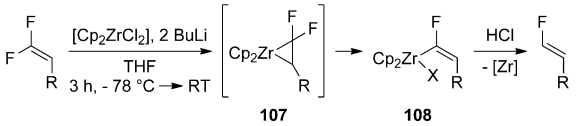


Scheme 26. Gold-catalyzed HDF: Net reaction (top, *t*BuXantphos = 4,5-bis(di-*tert*-butylphosphino)-9,9-dimethylxanthene; DCE = 1,2-dichloroethane; R = Me) and suggested mechanism (bottom, P∪P = Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene).

added. Mechanistic studies indicate a cationic Au^I complex **103** as the active species (Scheme 26). DFT calculations on the HDF of pentafluoropyridine suggest a direct oxidative addition mechanism via a three-centered transition state **104** to give the *cis*-Au^{III}(fluorido)(pyridyl) complex **105**. Upon reaction with the silane, intermediate **105** is believed to undergo reductive elimination in a single step via the unusual five-membered transition state **106**. Further experimental studies are desirable to fully understand and extend this high-potential catalyst system.

5.2. Olefinic Substrates

Hydrodefluorination of fluoroalkenes by oxidative addition is, to tour knowledge, limited to a single example which was reported by Ichikawa, Minami et al.[59] Several difluorovinylethers react at low temperature with in situ generated "zirconocene" to afford selectively the *E*-1-fluorovinylzirconocene **108**, presumably via formation of a zirconacyclopropane intermediate **107** (Scheme 27). Subsequent protonolysis



Scheme 27. Hydrodefluorination of fluoroalkenes by oxidative addition to a low-valent zirconium complex (R = OCH_2CH_2OMe, OPh, *p*-$OC_6H_4CH_3$, *p*-$OC_6H_4NMe_2$; X = F, Cl, CF = CHR).

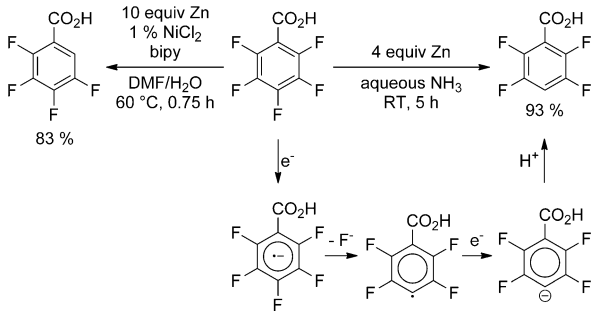
liberates the *E*-1-fluorovinylether. Alternatively, transmetalation of **108** with zinc iodide generates the corresponding (fluorovinyl)zinc iodide, which can be used for Negishi-type cross-coupling. Given the complex mixture of reactive species present in solutions of the "zirconocene" reagent,[60] mechanistic details remained unknown. Notably, oxidative addition of fluoroarenes to low-valent Group 4 metallocenes has several precedents.[5a,61]

6. Reductive Hydrodefluorination

The low-lying σ*-orbitals of fluorocarbons have early been recognized as a possible Achilles' heel for the carbon–fluorine bond.[62] Single electron transfer to the substrate LUMO generates a radical anion, which decomposes by fluoride elimination. The resulting radical is quenched by hydrogen-atom transfer or further reduction followed by protonation. In contrast to the previous reaction profiles, formation of a metal–carbon or a metal–fluorine bond is not necessarily involved.

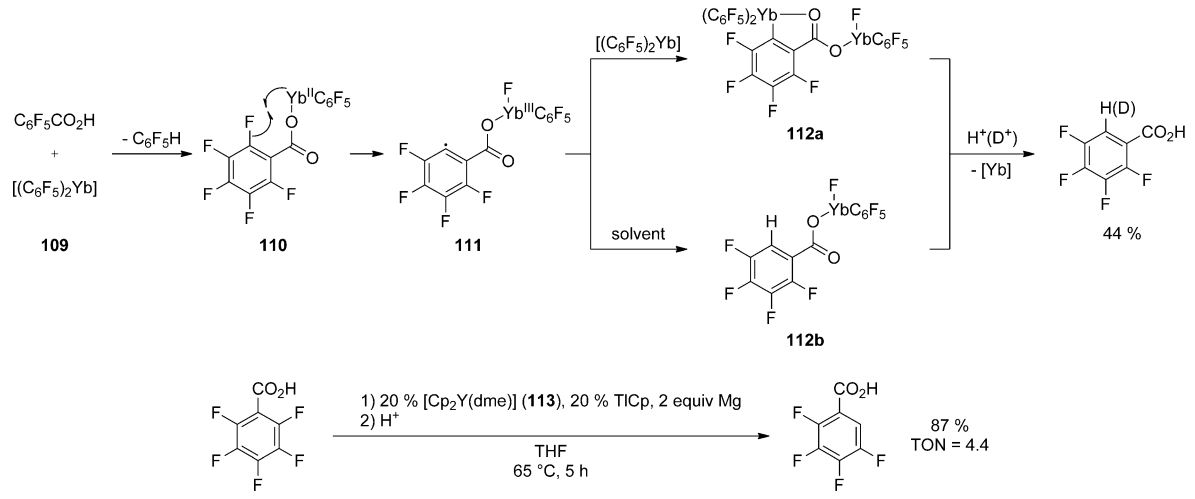
6.1. Aromatic Substrates

The use of zinc as an effective reducing agent for aromatic hydrodefluorination has been the subject of thorough studies by the groups of Shteingarts,[63] Platonov,[64] Starichenko,[65] and Adonin.[66] Most of this work is covered by two excellent Review articles.[67] Therefore only selected examples are highlighted herein. A broad range of substituted and unsubstituted fluoroarenes undergo HDF upon reduction with elemental zinc; substituents include alkyl, aryl, hydroxyalkyl, carboxy, carboxamide, and N-carboxylamino groups. The preferred charge localization in the initially formed radical anion determines the regioselectivity of subsequent fluoride elimination to generate an aryl radical.[63d,h] Transfer of a second electron reduces the radical to a carbanion that is finally protonated by an external proton source (Scheme 28). If the electron transfer, however, proceeds via a suitable transition-metal complex, the regioselectivity can be altered by directing groups. Several nickel complexes catalyze the reductive HDF of functional pentafluorobenzene derivatives with a marked *ortho*-selectivity. Although mechanistic details are unknown, a reaction sequence has been suggested comprising C–F bond oxidative addition to an in situ generated Ni^0 species followed by hydrolysis and reduction of the resulting Ni^{II} product.[66d]



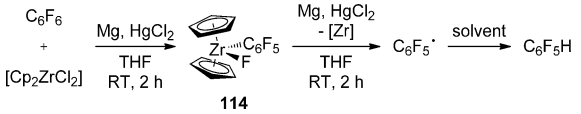
Scheme 28. Reductive hydrodefluorination of perfluorobenzoic acid with and without metal salt catalysis (bipy = 2,2′-bipyridyl; DMF = *N*,*N*-dimethylformamide).

Deacon et al. reported on the formation of 2,3,4,5-tetrafluorobenzoic acid upon treating pentafluorobenzoic acid with $[Yb(C_6F_5)_2]$ (**109**) followed by acidolysis (Scheme 29);[68] related reactivities have also been reported for YbI_2 and $[Cp^*_2Yb(OEt_2)]$.[69] A detailed study attributed the *ortho* selectivity to a directing effect of the carboxy moiety (Scheme 29). Protonolysis of an ytterbium–carbon bond in **109** presumably yields the carboxylate **110**. Subsequent intramolecular single-electron transfer to an *ortho*-fluorine substituent is believed to result in fluoride elimination and formation of the Yb^{III} aryl radical **111**, which further reacts by two competing pathways: Reduction by another equivalent of Yb^{II} affords the dinuclear aryl complex **112a**, whereas hydrogen abstraction from the solvent leads to the mononuclear species **112b**. Both intermediates liberate the HDF product upon hydrolysis, but only **112a** yields the deuterated product when D_2O is used; this is consistent with the experimentally observed partial deuterium incorporation. By adding a co-reductant, the Yb^{III} formed can be reconverted into Yb^{II}. The complex $[Cp_2Yb(dme)]$ (**113**, dme = 1,2-dimethoxyethane) was shown to catalyze the *ortho*-selective HDF of perfluoro- and 2,5-difluorobenzoic acid in the presence of excess magnesium and a Cp source (Scheme 29).[70]



Scheme 29. *ortho*-Selective reductive HDF of perfluorobenzoic acid by ytterbium(II) complexes. Top: Proposed mechanism; bottom: Catalytic reaction in the presence of a reducing agent (dme = 1,2-dimethoxyethane).

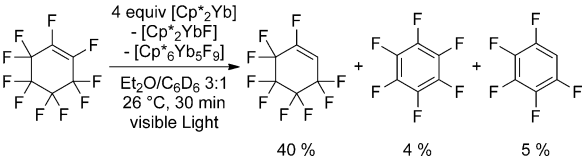
Group 4 metallocenes were also suitable for mediating reductive hydrodefluorination of perfluorobenzene and perfluoronaphthalene using magnesium/$HgCl_2$ as a reducing agent.[71] Oxidative addition of the substrate to an in situ generated M^{II} metallocene is believed to yield a $[Cp_2M^{IV}(F)(aryl)]$ complex **114** (Scheme 30). Subsequent electron transfer from the reducing agent induces metal–carbon bond fission and liberates an aryl radical. The complex **114** prepared independently exhibits a similar reactivity. The aryl radical abstracts hydrogen from the solvent to afford the HDF product. Accordingly, only deuterated products are obtained, when the reaction is performed in a deuterated solvent. Although the fate of the zirconium complex is not clear, this system can be used for a catalytic defluorination of fluorocarbons, suggesting that further reduction steps regenerate the low-valent zirconocene. Related catalytic systems consisting of $[Cp_2TiCl_2]$/$HgCl_2$/Mg or $[Cp_2ZrCl_2]$/PMe_3/Mg are similarly suitable.



Scheme 30. Reductive aromatic HDF mediated by a Group 4 metallocene.

6.2. Olefinic Substrates

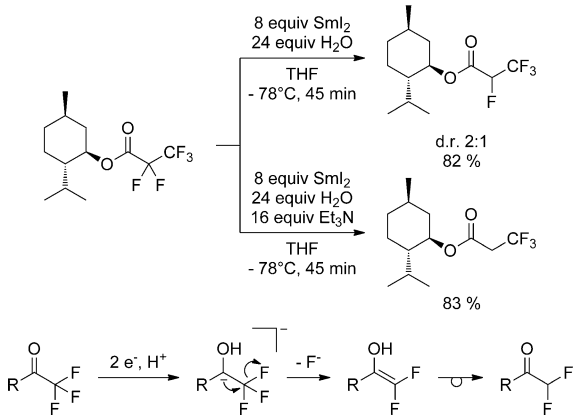
Examples of reductive alkene HDF are very sparse and limited to the application of rare-earth metallocenes.[69,72] Perfluorocyclohexene reacts with $[Cp^*_2M]$ (M = Yb, Eu, Sm) to give a mixture of HDF and defluorination products and the corresponding metallocene(III) fluoride (Scheme 31).[72] A closer look at the organometallic reaction products revealed the formation of mixed-valence metal fluorido clusters. Isotopic labeling studies suggest that the Cp* ligands and not the solvent are the hydrogen source. Interestingly, irradiation of the reaction mixture with visible light accelerates the reaction significantly. This has been attributed to a charge-transfer transition generating an excited metal complex with a higher reduction potential. A correlation between reduction potential and reaction rate was confirmed experimentally.



Scheme 31. A rare case of reductive HDF of an olefin.

6.3. Aliphatic Substrates

Transition-metal mediated reductive HDF of aliphatic substrates is hardly explored, mainly because inexpensive main-group metals, such as magnesium, are suitable for this purpose.[5i,o] In addition, reduction of aliphatic fluorides often results in undesired defluorination to give alkenes.[5] Hilmersson et al. have demonstrated that C–F bonds in the position α to ester and amide groups are selectively mono- or bis-hydrodefluorinated by samarium diiodide (Scheme 32).[73]



Scheme 32. Selective reductive aliphatic HDF using samarium diiodide: Examples and proposed mechanism.

Quite remarkably, a menthol-derived ester underwent a diastereoselective hydrodefluorination. Although the diastereomeric excess of 33% is not sufficient for synthetic applications, this approach demonstrates a novel strategy for the construction of fluorinated stereocenters by introducing an auxiliary for chiral induction in a subsequent HDF step. It was suggested that the reaction proceeds via initial electron transfer to the carbonyl π-system followed by protonation and a second electron transfer. The resulting carbanion is prone to α-fluoride elimination to afford an enol, which isomerizes to the HDF product. However, a possible directing effect of metal coordination to the carbonyl group was not taken into account.

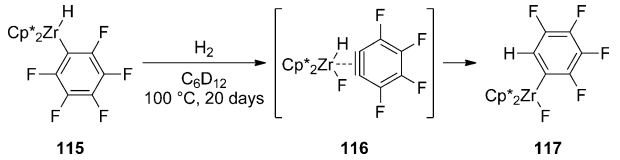
7. Intramolecular Hydrodefluorination

Many of the intermolecular transformations presented in the previous Sections involve an intramolecular HDF as the key step. This Section highlights selected examples of intramolecular HDF for which there is no corresponding intermolecular reaction. These intramolecular routes might offer alternative C–F activation pathways that could inspire the development of new intermolecular reactions. Hydrido ligands can act as a hydrogen source for the hydrodefluorination of a metal-bound fluorine-containing moiety. Since the introduction of certain fluoroalkyl groups into a metal's coordination sphere can be fairly straightforward, intramolecular HDF might offer a new approach to C–F bond

functionalization, especially for highly resistant aliphatic C–F bonds.

7.1. Aryl Ligands

Thermally induced exchange involving the hydrido ligand and a fluorine substituent in the *ortho* position of the zirconium pentafluorophenyl hydrido complex **115** was reported by Jones and co-workers (Scheme 33).[74] Trapping

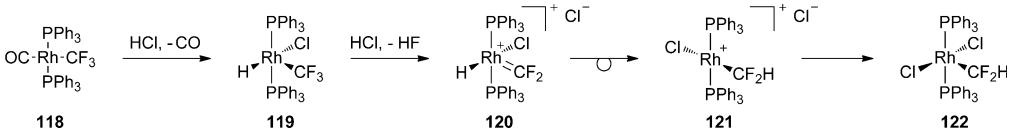


Scheme 33. Intramolecular HDF at a zirconium aryl complex.

experiments support the formation of an intermediate tetrafluorobenzyne complex **116** by β-fluoride elimination, again demonstrating the high exothermicity of Zr–F bond formation. Subsequent aryne insertion into the Zr–H bond yields the product **117**. A related difluorophenyl complex shows the same reactivity.[10c]

7.2. Alkyl and Alkylidene Ligands

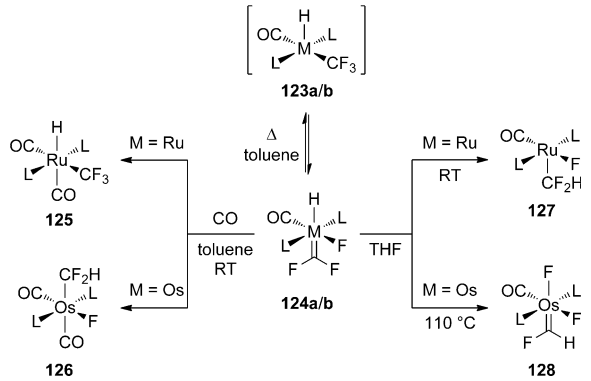
The conversion of fluorinated alkyl into carbene ligands has been known since Roper's pioneering work on Group 8 and 9 difluorocarbene complexes.[75] The rhodium(I) trifluoromethyl complex **118** was found to afford the rhodium(III) difluoromethyl complex **122** upon treatment with hydrogen chloride (Scheme 34).[75d] Detailed mechanistic studies indi-



Scheme 34. Intramolecular HDF at a rhodium trifluoromethyl complex.

cate the formation of the rhodium(III) hydrido complex **119**, which loses fluoride under acidic conditions to afford the cationic difluorocarbene hydrido complex **120**. Subsequent hydride migration to the carbene ligand and trapping of the difluoromethyl complex **121** with chloride yields the intramolecular HDF product **122**.

Under aprotic conditions, fluoride abstraction can also proceed intramolecularly provided that the metal center is sufficiently Lewis acidic. Caulton et al. observed reversible α-fluoride elimination in high-temperature equilibria between the trifluoromethyl complexes **123a**,**b** and their difluorocarbene fluorido isomers **124a**,**b**. The reaction profile is markedly influenced by the nature of the metal center (Scheme 35). Treatment of a solution of the ruthenium

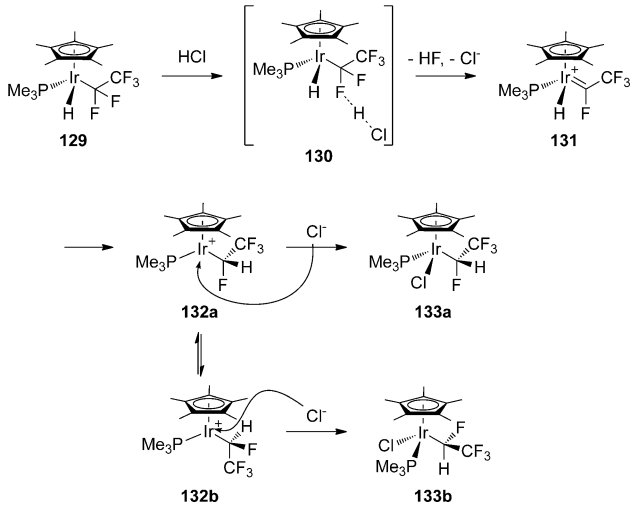


Scheme 35. Intramolecular HDF by reversible carbon–fluorine bond cleavage at Group 8 complexes (L = P*t*Bu$_2$Me, M = Ru, Os).

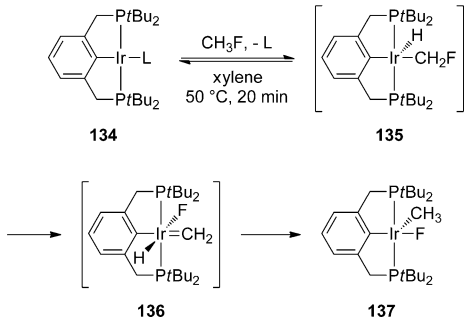
carbene complex **124a** with CO induces an irreversible fluoride migration to give the coordinatively saturated trifluoromethyl complex **125**, whereas the osmium congener **124b** undergoes a hydride migration to yield the difluoromethyl complex **126**. When a weaker ligand such as THF is used, **124a** can also undergo hydride migration to yield the five-coordinate difluoromethyl complex **127**. In the case of osmium, the five-coordinate difluoromethyl complex is not stable and undergoes another α-fluoride elimination to afford the monofluorocarbene complex **128**. Based on DFT calculations, these differences in reactivity were attributed to the osmium atom's preference for higher oxidation states and its higher Lewis acidity.

Related chemistry at fluorinated iridium half-sandwich complexes has been thoroughly investigated by Hughes et al.[76] Treatment of the hydrido pentafluoroethyl complex **129** with an acid yields the tetrafluoroethyl complexes **133a**,**b** (Scheme 36).[77] A considerable diastereoselectivity was observed in these reactions. Detailed mechanistic studies revealed the initial protonation of a fluorine substituent at the α-carbon to be strongly influenced by the preferred conformation of the pentafluoroethyl moiety.[78] Subsequent hydrogen fluoride elimination yields the cationic perfluoroalkylidene complex **131**. Subsequently, the hydrido ligand migrates stereospecifically to form the cationic tetrafluoroethyl complex **132a**. The relative rates of inversion at iridium and irreversible trapping with chloride determine whether the kinetic product **133a** or its diastereomer **133b** is formed. They are strongly dependent on solvent effects, chloride concentration, and the presence of Lewis acids.

The combination of intramolecular α-fluoride elimination and hydride migration with intermolecular C–H bond oxidative addition resulted in a formal intermolecular C–F bond oxidative addition. Goldman et al. showed that the iridium(I) pincer complex **134** reacts with fluoromethane to afford the Ir^{III} methyl fluorido complex **137** (Scheme 37).[79] Mechanistic investigations indicate the initial formation of



Scheme 36. Intramolecular HDF at an iridium perfluoroalkyl complex (an analogous mechanism exists for the enantiomer).



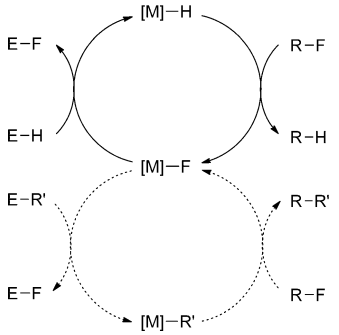
Scheme 37. Intramolecular HDF at iridium combined with intermolecular C–H activation to an overall C–F oxidative addition (L = norbornene).

the fluoroalkyl hydrido complex **135** by reversible C–H oxidative addition. Subsequent α-fluoride elimination yields the carbene complex **136** which by hydride migration converts into the methyl fluorido complex **137**. Although this reaction is limited to monofluorinated substrates without hydrogen atoms in the β-position, this sequence demonstrates a new approach to the challenge of aliphatic C–F bond oxidative addition.

8. Conclusion and Outlook

The hydrodefluorination reaction is on the verge of becoming a synthetic tool for deriving partially fluorinated building blocks from readily available bulk chemicals. Whereas most studies to date are mainly concerned with achieving HDF reactivity, future work will have to focus on controlling HDF selectivity. The mechanistic variability of HDF reactions is remarkable and triggered by several parameters that will provide important means to optimize HDF reagents.

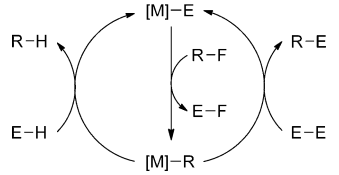
The generation of strong metal–fluorine bonds can promote fluorido complex formation by H/F exchange



Scheme 38. Schematic representation of the catalytic cycles for HDF (top) and a hypothetical cross-coupling (bottom) by fluorido complex formation (R–F = substrate, [M]–H = hydrido complex, [M]–F = fluorido complex, E–H = hydride reagent or H_2, E–R′ = alkylating reagent, E–F = spent hydride/alkylating reagent).

involving a hydrido complex and a fluorinated substrate. A catalytic process requires reconversion of the fluorido complex into a hydrido species by an external hydride reagent (Scheme 38). The M–F bond strength can be altered by adjusting the metal center's Lewis acidity to avoid the generation of overly stable fluorido complexes, which can hamper catalytic applications. The hydrido ligand's preference for attack at either the carbon atom or the fluorine atom of the C–F bond is decisive for the overall HDF regioselectivity. Despite recent improvements in catalytic C–F activation via fluorido complex formation, further developments of this reaction profile beyond HDF are challenging. A putative catalytic cycle for cross-coupling would require exchange of a metal-bound alkyl group for a substrate fluorine substituent (Scheme 38). The considerable differences between metal–hydrogen and metal–carbon bonds render this approach challenging.

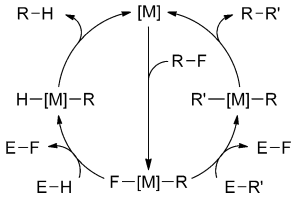
At metal centers with a lower affinity towards fluorido ligands, C–F bond activation can result in metal–carbon bond formation and a transfer of the fluorine substituent to a fluorophilic moiety, such as a boryl, silyl, or hydrido ligand. Cleavage of the metal–carbon bond by an external hydrogen source liberates the HDF product and regenerates the fluorophilic ligand, thus completing the catalytic cycle (Scheme 39). This fluorine-accepting ligand provides the driving force by forming a strong bond to fluorine. In addition, this ligand is often Lewis acidic and can influence the reaction route; this effect may be further exploited for



Scheme 39. Schematic representation of the catalytic cycle for HDF (left semicircle) and functionalization (right semicircle) by metal–carbon bond formation (R–F = substrate, [M]–E = metal complex bearing a fluorophilic ligand E, [M]–R = intermediate complex, E–H = hydrogen source, E–E = functionalizing reagent, e.g. a diborane, E–F = spent hydrogen source/functionalizing reagent).

controlling the HDF regioselectivity. The intermediate formation of a metal–carbon bond provides a plethora of possibilities for functionalization of the fluorinated moiety, such as silylation and borylation, and might potentially be further exploited for cross-coupling reactions.

Low-valent metal centers capable of a two-electron oxidation can form both metal–carbon and metal–fluorine bonds simultaneously by oxidative addition of a substrate carbon–fluorine bond. Subsequent conversion of the metal–fluorine bond to a metal–hydrogen bond by a hydrogen source allows for reductive elimination of the HDF product and regeneration of the low-valent metal complex (Scheme 40). Conversion of the metal–fluorine bond into

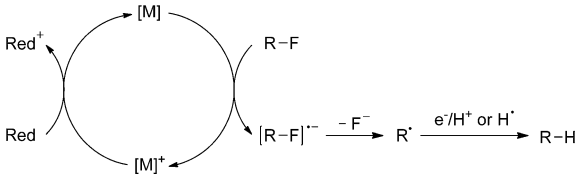


Scheme 40. Schematic representation of the catalytic cycle for HDF (left semicircle) and cross-coupling (right semicircle) via oxidative addition of a C–F bond (R–F = substrate, [M] = low-valent metal complex, F–[M]–R = oxidative addition product, E–H = hydrogen source, E–R′ = alkylating reagent, E–F = spent hydrogen source/alkylating reagent).

a metal–carbon bond enables reductive elimination of a cross-coupling product. A systematic extension of these reactions is expected to furnish a versatile means for constructing fluorinated building blocks. Despite numerous mechanistic investigations, several distinct pathways remain the subjects of discussion. Future mechanistic studies will need more sophisticated models.

Neither metal–carbon nor metal–fluorine bonds are necessarily formed, if the low-valent metal center prefers to undergo a one-electron oxidation. Single-electron transfer to a low-lying LUMO can generate a substrate radical anion. Fluoride elimination from the carbon atom with the highest charge localization yields a substrate radical that is finally quenched to afford the HDF product. Since charge localization in a free-radical anion depends solely on the substrate structure, controlling the regioselectivity is only possible by introducing a directing group that anchors the metal complex and directs the electron transfer to a specific C–F bond. A chiral directing group can induce diastereoselectivity. An external reducing agent can regenerate the low-valent metal center thus enabling a catalytic process (Scheme 41). The low cost and high functional-group tolerance make this profile highly promising. Applications beyond hydrodefluorination have not been reported, but may be achieved by applying classical organic free-radical chemistry to the generated substrate radical.

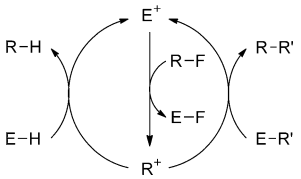
In complexes bearing both a hydrido and a fluorinated organic ligand, hydrodefluorination can proceed intramolecularly. Hydride migration from the metal atom to the ligand requires the generation of an electrophilic carbon atom by



Scheme 41. Schematic representation of the catalytic cycle for reductive HDF (R–F = substrate, [M] = low-valent metal complex, $[M]^+$ = oxidized metal complex, Red = reducing reagent, Red^+ = spent reducing reagent).

external fluoride abstraction or by fluoride migration to the metal center. If the enthalpies of carbon–fluorine and carbon–hydrogen bonds differ only slightly from those of metal–fluorine and metal–hydrogen bonds, respectively, migration can be reversible. Despite the lack of direct synthetic applications, these transformations provide an approach to cleave highly resistant aliphatic carbon–fluorine bonds by tethering fluorinated alkyl groups to a metal's coordination sphere for example, by oxidative addition of a more labile adjacent bond. Moreover, chiral induction from the metal center can enable stereospecific hydride migration. The reversibility could, in principle, also be exploited to achieve selective fluorination.

With this well-documented foundation at hand, HDF might be established as a synthetically useful tool. The substrate scope has so far been too limited for most practical applications. For the synthesis of simple hydrofluorocarbons by the HDF of fluorinated bulk chemicals, this limitation might be acceptable provided that inexpensive H_2 is used as the hydrogen source and the catalysts' efficiencies can be increased by several orders of magnitude. For the synthesis of partially fluorinated fine chemicals, in contrast, the HDF catalyst system will have to be compatible with an extended substrate scope and must exhibit a high regioselectivity. It is noteworthy that recent work on main-group Lewis acids achieved remarkable efficiencies in the hydrodefluorination and cross-coupling of aliphatic fluorides.[5h,39] Strong Lewis acids, such as silylium ions, alumylium ions, and fluorinated boranes, can cleave aliphatic C–F bonds heterolytically to generate a substrate carbocation. This carbocation can abstract hydride from a silane to give the HDF product and regenerate an active silylium cation, thus completing a catalytic HDF cycle (Scheme 42, left semicircle). Cross-coupling has been achieved by reaction of the carbocation with



Scheme 42. Schematic representation of the catalytic cycle for HDF (left semicircle) and cross-coupling (right semicircle) at main-group Lewis acids (R–F = substrate, E^+ = Lewis acid, E–H = hydrogen source, E–R′ alkylating reagent, E–F = spent hydrogen source/alkylating reagent).

a trialkylaluminum reagent, which by transfer of a carbanionic alkyl group to the substrate forms a Lewis acidic alumylium cation that completes the catalytic cycle.

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) within the Research Training Group GRK 1582/1 "Fluor als Schlüsselelement (Fluorine as a Key Element)". M.F.K. and T.B. thank the Humboldt-Universität zu Berlin for funding. M.F.K. and D.L. thank the Freie Universität Berlin for funding. M.F.K. is grateful to the Deutscher Akademischer Austauschdienst (DAAD) for a conference scholarship. M.F.K. thanks Paul Kläring for photography.

Received: July 4, 2012
Published online: January 25, 2013

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